PTO 05-2517

CY=DE DATE=19950629 KIND=C1
PN=4 419 816

AGGREGATE CONTAINING TITANIUM AND ITS USE TO INCREASE THE DURABILITY OF THE REFRACTORY LINING OF A FURNACE AND AS A SLAG-MAKING FLUX [TITANHALTIGER ZUSCHLAGSTOFF UND DESSEN VERWENDUNG ZUR ERHÖHUNG DER HALTBARKEIT DER FEUERFESTEN AUSMAUERUNG EINES OFENS UND ALS SCHLACKENBILDNER]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. March 2005

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(10):	DE
DOCUMENT NUMBER	(11):	44 19 816
DOCUMENT KIND	(12):	C1
PUBLICATION DATE	(43):	19950629
APPLICATION NUMBER	(21):	P 44 19 816.7-24
APPLICATION DATE	(22):	19940607
INTERNATIONAL CLASSIFICATION	(51):	C 21 B 3/02; C 04 B 28/02; C 21 B 7/06; F 27 D 1/16; C 21 C 5/44; C 21 C 5/36; C 22 B 1/14
PRIORITY COUNTRY	(33):	NA
PRIORITY NUMBER	(31):	NA
PRIORITY DATE	(32):	NA
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TITLE	(54):	AGGREGATE CONTAINING TITANIUM AND ITS USE TO INCREASE THE DURABILITY OF THE REFRACTORY LINING OF A FURNACE AND AS A SLAG-MAKING FLUX
FOREIGN TITLE	[54A]:	TITANHALTIGER ZUSCHLAGSTOFF UND DESSEN VERWENDUNG ZUR ERHÖHUNG DER HALTBARKEIT DER FEUERFESTEN AUSMAUERUNG EINES OFENS UND ALS SCHLACKENBILDNER

Description

The present invention relates to an aggregate containing titanium and its use to increase the durability of the refractory lining of a furnace and as a slag-making flux.

In the iron, steel and casting industry, fairly large quantities of ilmenite are used as a titanium-carrier aggregate for furnaces, especially blast furnaces. Usually, the natural ilmenite is crushed into pieces with a size of about 50 mm and is placed directly into the furnaces. The addition of ilmenite causes the nitrogen content in the raw iron to be bound in the form of titanium nitrides and titanium carbonitrides. In this way, the removal of nitrogen from the metallic melts is achieved. Because of partial depositing of the titanium compounds formed in this way on the internal walls of the refractory linings of the furnaces, especially in the hearth of blast furnaces, the durability of the linings is increased. However, natural ilmenite is obtained at great expense, whereby natural resources of high-quality ilmenite are reduced.

An aggregate containing titanium for furnaces, consisting of residues of TiO_2 manufacturing and one or more constituents selected from coal or residues containing coal, iron, iron oxide or residues containing iron or iron oxide is known from DE 43 04 724 C1.

In the iron, steel and casting industry, aggregates are also put into the furnaces as slag-making flux. The aggregates are compounds and mixtures occurring in nature, which contain e.g. the oxides CaO, Al_2O_3, SiO_2 and MgO. These aggregates must be purchased at great

expense for their use as slag-making flux.

The object of the present invention is to provide an aggregate containing titanium, in a cost-effective and environmentally friendly manner, as a substitute for the natural ilmenite used in metallurgical processes and as a substitute for the natural slag-making fluxes used as aggregates.

The object on which the present invention is based is achieved with an aggregate containing titanium, consisting of residues from TiO_2 manufacturing and one or more constituents selected from among coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide and one or more constituents selected from earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

Residues from the manufacturing of titanium dioxide, especially of titanium dioxide pigments, can advantageously be processed according to the invention with residues containing coal, iron or iron oxide and with residues containing earth alkali metal oxide, earth alkali metal hydroxide or residues containing Al_2O_3, $Al(OH)_3$ or SiO_2. These residues will no longer be sent to landfills, but according to the invention they will be recycled economically.

The object on which the present invention is based is further achieved by an aggregate containing titanium, consisting of residues from TiO_2 manufacturing and one or more constituents selected from

earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

According to the invention, residues from manufacturing of titanium dioxide, especially of titanium dioxide pigments can be advantageously processed with residues containing earth alkali metal oxides, earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or SiO_2. These residues will no longer be sent to landfills, but according to the invention they will be recycled economically.

A preferred embodiment of the invention is an aggregate containing titanium, consisting of 30 to 70 weight-% of residues from TiO_2 manufacturing, 5 to 50 weight-% coal or residues containing coal and 20 to 65 weight-% earth alkali metal oxides, earth alkali metal hydroxides or residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

This composition according to the invention is well suited for repair of thin refractory linings in furnaces. Good results are also obtained with this composition as a slag-forming flux.

A preferred embodiment of the invention is an aggregate containing titanium, consisting of 30 to 70 weight-% of residues from TiO_2 manufacturing, 5 to 50 weight-% iron, iron oxide or residues containing iron or iron oxide and 20 to 65 weight-% of earth alkali metal oxides, earth alkali metal hydroxides or residues containing

earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

This composition according to the invention is also especially good for repair of thin refractory linings in furnaces. Good results are also obtained with this composition as a slag-forming flux.

A preferred embodiment of the invention is an aggregate containing titanium, consisting of 50 to 95 weight-% of residues from TiO_2 manufacturing, 5 to 50 weight-% of earth alkali metal oxides, earth alkali metal hydroxides or residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

This aggregate containing titanium according to the invention is well suited for repair of thin refractory linings in furnaces. Very good results are obtained with this composition as a slag-forming flux. Very good results are obtained in adjusting the slag basicity with CaO and residues containing CaO. In this process, the binding of sulfur and phosphorous as calcium-containing sulfur and phosphorous compounds is achieved to a great extent. Due to the addition of MgO and residues containing MgO, good results are also achieved in increasing the degree of saturation in the slag formed. In this way, the dissolving of MgO contents from the refractory lining can be prevented. Good results as a slag-forming flux are obtained with residues containing Al_2O_3 or $Al(OH)_3$. These residues exhibit very good results as fluxing agents for limestone slag. An acceleration of the

dissolving of lime is thereby achieved. With residues containing SiO_2, very good results are achieved as slag-forming flux. In the aggregate mentioned above containing titanium, according to the invention, it is a case of powder mixture having a grain size from 50 to 5000 μm.

A preferred embodiment of the invention is an aggregate containing titanium in the form of sintered elements. The sintered elements are produced in that the components are mixed, the homogeneous mixture is put into a sintering mold and then sintered in a known way. The sintered material can be broken to the desired size. In addition to good breakage strength, the sintered elements according to the invention exhibit very good results as slag-forming flux. Good results have been achieved with these sintered elements in increasing the durability of the refractory lining of a furnace.

The object on which the present invention is based is further achieved by an aggregate containing titanium consisting of residues of TiO_2 manufacturing, one or more binders and one or more constituents selected from among coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide and one or more constituents selected from earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2 in the form of briquettes, pellets or granulates. With this aggregate containing titanium according to the invention, very good results are achieved with respect to breakage strength. With this molded element according

to the invention, good results are achieved as a slag-forming flux and good results are obtained in increasing the durability of the refractory lining of a furnace. The molded element according to the invention can be subsequently treated at temperatures of 100°C to 1000°C. The molded element designed as a briquette can be cylindrical, round, oval, in the shape of a parallelipiped or cuboid.

The object on which the present invention is based is further achieved by an aggregate containing titanium consisting of residues of TiO_2 manufacturing, one or more binders and one or more constituents selected from among earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2. With this aggregate containing titanium according to the invention, very good results are achieved with respect to breakage strength. With this molded element according to the invention, good results are achieved as a slag-forming flux and good results are obtained in increasing the durability of the refractory lining of a furnace.

A preferred embodiment of the invention is an aggregate containing titanium, containing 2 to 30 weight-% binder. With this binder, very good results are obtained with respect to the breakage strength of the molded elements.

A preferred embodiment of the invention is an aggregate containing titanium, whereby the binders are Portland cement, blast furnace cement, aluminous cement or fly ash. According to the

invention, all available hydraulic, ceramic and chemical binders, as well as swelling binder, can be used as binders.

According to the invention, the use of an aggregate containing titanium as a powder mixture or in the form molded elements is provided for introduction into a furnace for increasing the durability of the refractory lining of a furnace and as a slag-forming flux in the iron, steel and casting industry.

The invention will now be explained in more detail using an example.

Example

Into a mixer, 50 weight-% treatment residue from TiO_2 pigment manufacturing according to the sulfate method, containing 50 weight-% TiO_2, 23 weight-% SiO_2, 5 weight-% Al_2O_3, 6 weight-% CaO and 5 weight-% Fe_2O_3, as well as 12 weight-% residue containing CaO with 95 weight-% CaO content (calculated on the dry substance), and 18 weight-% residue containing MgO with 89 weight-% MgO residue (calculated on the dry substance) were placed. Then, added to this during stirring, were 13 weight-% blast furnace cement, containing 51 weight-% CaO, 27 weight-% SiO_2, 4.5 weight-% Al_2O_3, 4.5 weight-% TiO_2, 1.5 weight-% Fe_2O_3, 0.5 weight-% Mn_2O_3 and 3.5 weight-% MgO, as well as 1.5 weight-% electrostatic filter ash, containing 50 weight-% SiO_2, 28 weight-% Al_2O_3, 7 weight-% Fe_2O_3, 3.2 weight-% CaO, 2.2 weight-% MgO, 3.8 weight-% K_2O and 0.9 weight-% Na_2O and 5.5 weight-% aluminous cement, containing 40 weight-% CaO, 6.5 weight-% SiO_2, 25 weight-% Al_2O_3, 25 weight-% TiO_2, 1.0 weight-% Fe_2O_3, 0.1 weight-% Mn_2O_3 and 1.0 weight-%

MgO and the mixture was mixed thoroughly for 5 minutes. 50 weight-parts of this mixture were mixed with 50 weight-parts of water. The aqueous mixture was homogenized for 2 minutes. The homogeneous mixture was placed on a briquette press. A pressure of 120 bar was set on the briquette press, whereby cylindrical molded elements (briquettes) with an outer diameter of 80 mm and a length of 40 mm were obtained. After a setting time of 14 days, the molded elements exhibited a breakage strength of 2950 N and a breakage strength of 3150 N after heating to 1000°C for one and one-half hours in 100% CO atmosphere. The cylindrical molded elements (briquettes) have the following composition:

Constituents	Percentages (Weight-%)
TiO_2	25.1
SiO_2	25.9
MgO	16.4
CaO	22.8
Al_2O_3	5.2
Fe_2O_3	2.5
Na	0.1
K	0.07
Remaining constituents	1.93

To determine the breakage strength (spot strength), the molded elements are exposed, in a test press, to a continuously increasing force acting on them until they break. The force acting on the molded element when it breaks is the measurement of its breakage strength.

Patent Claims

1. Aggregate containing titanium, consisting of residues from TiO_2 manufacturing and one or more constituents selected from among coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide and one or more constituents selected from earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

2. Aggregate containing titanium, consisting of residues from TiO_2 manufacturing and one or more constituents selected from earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

3. Aggregate containing titanium according to Claim 1, consisting of 30 to 70 weight-% of residues from TiO_2 manufacturing, 5 to 50 weight-% coal or residues containing coal and 20 to 65 weight-% earth alkali metal oxides, earth alkali metal hydroxides or residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

4. Aggregate containing titanium according to Claim 1, consisting of 30 to 70 weight-% of residues from TiO_2 manufacturing, 5 to 50 weight-% iron, iron oxide or residues containing iron or iron oxide

and 20 to 65 weight-% of earth alkali metal oxides, earth alkali metal hydroxides or residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

5. Aggregate containing titanium according to Claim 2, consisting of 50 to 95 weight-% of residues from TiO_2 manufacturing, 5 to 50 weight-% of earth alkali metal oxides, earth alkali metal hydroxides or residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$ or residues containing Al_2O_3, $Al(OH)_3$, SiO_2 or residues containing SiO_2.

6. Aggregate containing titanium according to Claims 1 to 5, in the form of sintered elements.

7. Aggregate containing titanium consisting of residues of TiO_2 manufacturing, one or more binders and one or more constituents selected from among coal or residues containing coal, iron, iron oxide, residues containing iron or iron oxide and one or more constituents selected from earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2 in the form of briquettes, pellets or granulates.

8. Aggregate containing titanium consisting of residues of TiO_2 manufacturing, one or more binders and one or more constituents selected from among earth alkali metal oxides, earth alkali metal hydroxides, residues containing earth alkali metal oxides or earth

alkali metal hydroxides, Al_2O_3, $Al(OH)_3$, residues containing Al_2O_3 or $Al(OH)_3$ and SiO_2 or residues containing SiO_2.

9. Aggregate containing titanium according to Claims 7 and 8, containing 2 to 30 weight-% binder.

10. Aggregate containing titanium according to Claims 7 to 9, wherein the binders are Portland cement, blast furnace cement, aluminous cement or fly ash.

11. Use of an aggregate containing titanium as a powder mixture and/or in the form of molded elements according to Claims 1 to 10 to be placed in a furnace to increase the durability of the refractory lining of a furnace and as a slag-making flux in the iron, steel and casting industry.